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Chemical effects in Ag and Cr compounds studied by EDXRF, WDXRF and PIXE

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Abstract K X-ray intensity ratios of Ag and its compounds such as AgI, AgBr, AgCl, Ag_2SO_4, $AgNO_3$,and $AgCO_3$ and Cr and its compounds such as Cr_2O_3, $K_2Cr_2O_7$, K_2CrO_4, $CrSO_4$ and $CrCl_3$ were measured using 59.56 keV γ-rays emitted from ^{241}Am radioisotope source (EDXRF), X-ray photons from Rh X-ray tube (WDXRF) and protons from the 6MV FOTIA accelerator (PIXE) of energy 2.5 MeV and 5 MeV. The measured ratios in pure metal were compared with Scofield theoretical values. The ratio for K X-ray emission rates by photon excitation, X-ray and proton excitation showed variation for the compounds from the pure elements and for different modes of excitation.

Keywords : K X-ray intensity ratios, silver, chromium, EDXRF, WDXRF, PIXE, chemical structures

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1. Introduction

In X-ray emission analysis, an accurate knowledge of the X-ray intensity ratios is of great importance not only to verify and develop theoretical models describing fundamental ionization phenomena but also for obtaining accurate concentration values for elements while de-convoluting X-ray spectra. The relative intensities of X-ray lines, which originate from radioactive decays leading to the filling of the vacancies in the same sub-shells, are expected to remain constant irrespective of the mode of excitation. However, several investigators [1-5] have found that X-ray intensity ratios depend largely on the chemical state or rather the chemical environment of the X-ray emitting atom. The accurate measurement of K X-ray transition probabilities in different chemical compounds of any given element gives information about the influence of the chemical environment on the atom under consideration. In compounds, the existence of chemical effects on K X-ray intensity ratios has been reported [6-8]. These effects are interpreted in terms of valence electron distribution and chemical bonding. Brunner *et al* [9] tested the chemical effects sensitivity of the K X-ray intensity ratios by proton excitation for different $3d$ elements Cr, Mn, Fe and Cu. They explained their experimental results by the change in screening of $3p$ electrons by $3d$ valence electrons. Their values differed by 5% from those of pure elements. Sogut *et al* [10] have carried out measurements of K_β/K_α of Ag compounds and found a variation from 0.217-0.254 using EDXRF technique. A number of investigators have also reported the chemical effects on Cr and its compounds [11-14]. Kataria *et al* [15] have confirmed the dependence of intensity ratios to oxidation states for Mn using XRF technique and found a deviation of 10% from that of pure Mn. Finn Folkmann [16] has studied the chemical effects in Cr containing compounds by protons .We have carried out measurements of K_β/K_α ratios for Ag and Cr compounds using PIXE, XRF and WDXRF to study the dependence of this

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ratio on the various modes of excitation as well as the chemical effects.

2. Experimental methods

Ag metal and Ag compounds such as AgI, AgCl, AgBr, Ag_2SO_4, $AgCO_3$ and $AgNO_3$ were made into thin films of 200 $\mu g/cm^2$ (satisfying the condition $\mu t < 1$ where μ is the attenuation coefficient of the element under consideration (cm^2/gm) and t is the thickness in g/cm^2) on C backing of 25 $\mu g/cm^2$ by resistive heating evaporation technique. In the case of Cr, it is known that Cr exists in three main oxidation states, namely, zero (metal), three and six. Cr^{III} is an essential mammalian trace element whereas Cr^{VI} is toxic and individuals in contact with Cr^{VI} face serious health hazards [17]. In the light of the above facts, we have studied the influence of chemical structures on the K X-ray intensity ratios by measurements of X-ray yields of Cr metal (0) and Cr compounds such as Cr_2O_3 (III), $K_2Cr_2O_7$ (VI), K_2CrO_4 (VI), CrSO4 (III) and $CrCl_3$ (III). The Cr samples were powdered and pelletized for XRF studies. For the PIXE analyses, the Cr powder was placed on adhesive Scotch Tape and then mounted on the Al ladder for PIXE measurements. The samples were placed for the measurement of yield of K_α and K_β peaks by the following modes of excitation.

EDXRF:

The samples were excited by 100 mCi Am^{241} radioisotope source. The Ag X-rays were detected by Si (Li) detector of area $30mm^2$ and 3mm thickness and a Be window of 1mil thickness with a resolution of 170 eV at 5.9 KeV Mn K_α X-ray. Figure 1a gives the X-ray spectra of Ag metal by EDXRF. In the case of Cr, the compounds were powdered and homogenized with cellulose binder and subjected to a pressure of 15 tons/sq.inch by a hydraulic press to make pellets of 25 mm diameter. The X-ray spectra for Ag compounds were obtained for a counting time of 8000 seconds and the Cr compounds were obtained for a counting time of 2000 seconds and stored in 8k PCA card for further off-line analysis.

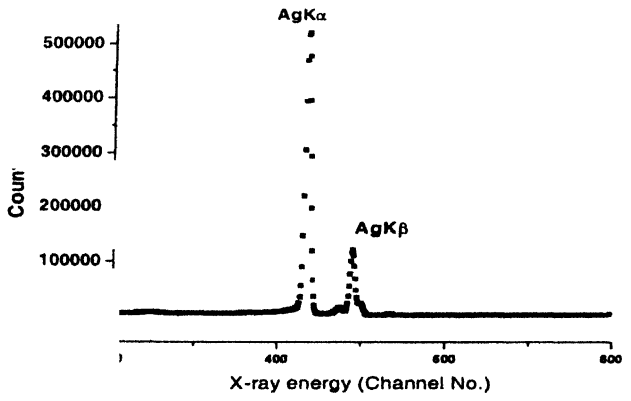


Figure 1a. X-ray spectrum of Ag metal film.

WDXRF:

Ag and Cr compounds were pelletized and placed in cubical ho and subjected to X-ray photons emitted from Rh target X r tube. The X-ray intensity was recorded in computer controll Philips #PW 2400 sequential X-ray spectrometer. The pow applied was 3KW. X-ray counts were obtained as smal time 25 seconds. They were then analyzed for K_α and K peaks

PIXE:

For the PIXE measurements, thin films for Ag compounds a Cr finely powdered samples mounted on an adhesive Scot tape were mounted on an aluminum ladder placed in the PIX chamber. A proton beam of 2.5 MeV energy and 5 MeV ener and 2nA current was directed on the targets and the X-ray coun were detected by a Si (Li) detector of resolution 170 eV at 5 KeV Mn K_α X-ray located at 90° to the incident beam. The ray spectra were obtained for a counting time of 6000 secon and stored for further off-line analysis.

3. Results and discussion

The X-ray spectra of Ag and AgI compound by EDXRF a PIXE are shown in Figures 1a and 1b and in Figures 2a and

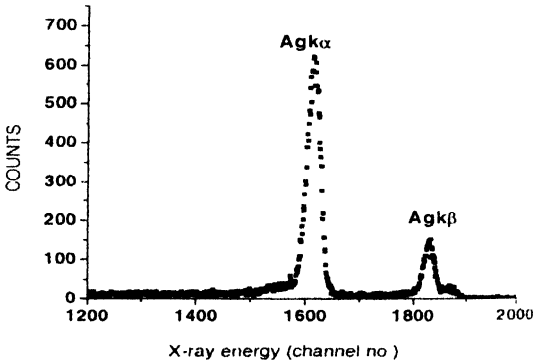


Figure 1b. PIXE X-ray spectrum of Ag metal film.

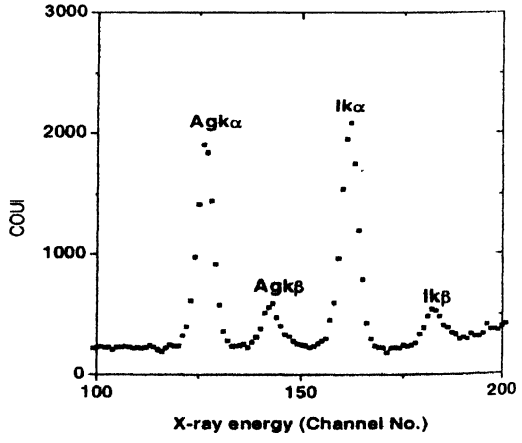
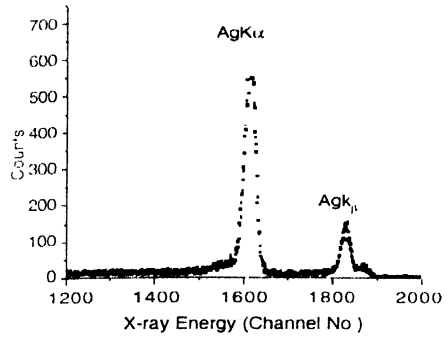
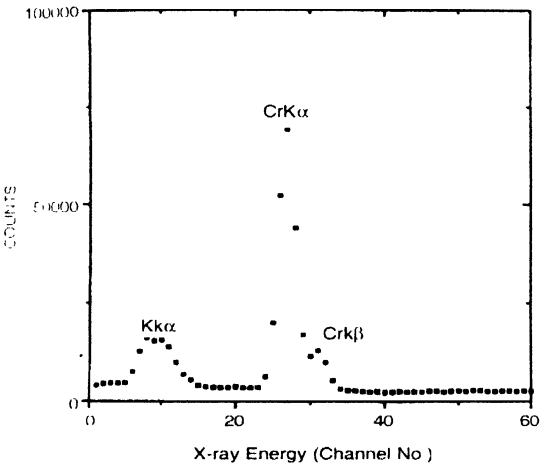


Figure 2a. X-ray spectrum of AgI compound.

The X-ray spectra of $K_2Cr_2O_7$ by EDXRF and $CrSO_4$ by PIXE are shown in Figures 3a and 3b respectively.



igure 2b. PIXE X-ray spectrum of AgI compound



igure 3a. X-ray spectrum of $K_2Cr_2O_7$ compound

I intensities were corrected for energy losses in Be window and excitation cum detection factors for K_β and K_α X-rays. In the case of pellets, correction for mass absorption coefficients of cellulose was taken into consideration. Table 1 gives a comparison of the intensity ratio values by EDXRF, WDXRF and PIXE and theoretical values and the measurements by Sogut *et al.* [10]. The K_β/K_α intensity ratio values were calculated using the relation

$$I(K_\beta)/I(K_\alpha) = N(K_\beta)/N(K_\alpha) * \varepsilon(K_\alpha)/\varepsilon(K_\beta) * \beta(K_\alpha)/\beta(K_\beta)$$

where $N(K_\alpha)$ and $N(K_\beta)$ are counts corresponding to K_α and K_β respectively; $\varepsilon(K_\alpha)$ and $\varepsilon(K_\beta)$ are the efficiencies of detector for K_α and K_β, respectively; $\beta(K_\alpha)$ and $\beta(K_\beta)$

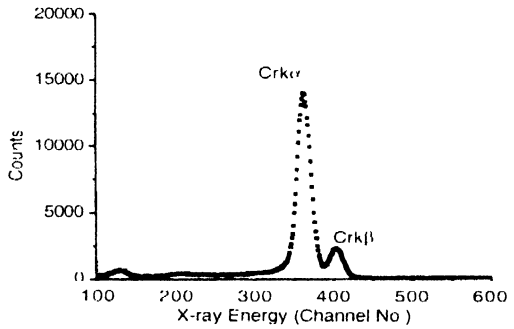


Figure 3b PIXE X-ray spectrum of $CrSO_4$ compound

are the target self-absorption correction factor for both the incident and emitted radiations which were calculated using the following equation

$$\beta = \left[1-\exp[(-1)]((\mu_{inc}/\cos\Phi)+\mu_{emt})t\right] / \left[((\mu_{inc}/\cos\Phi)+\mu_{emt})t\right],$$

where μ_{inc} (cm^2/g) and μ_{emt} (cm^2/g) are the mass attenuation coefficients at the incident photon energy and at the fluorescent X-ray energy of the sample, respectively and t (g/cm^2) is the measured mass thickness of the sample, Φ has been calculated by using the following expression

$$\cos\Phi = L/\left[L^2 + 0.25(R_0 + R_1)^2\right]^{1/2},$$

where L is the distance from source to the sample and R_0 and R_1 the internal and external diameters of radioisotope source

Table 1. K X-ray intensity ratios of Cr and its compounds

Compound	K_β/K_α photons EDXRF	Rebohle [21] photons XRF	Theoretical Scofield [18] photons	K_β/K_α X-rays WDXRF	K_β/K_α protons PIXE	Folkmann [16] protons PIXE	Valence state
K_2CrO_4	0.140±.003		0.137	0.173±.002	0 190±.001	0 1955± 0021	VI
$K_2Cr_2O_7$	0.142±.002	0.1544	0.140	0 172± 002	0.189±.002	0 1963± 0017	VI
Cr_2O_3	0.145±.003	0.1447	0.141	0 175± 002	0 180± 01	0.1752± 0014	III
Cr-Al	0 154±.002	0 147	0.147	——	———	——	0
$CrSO_4$	0.135±.003	——-	——-	0.171±.003	——-	——-	III
$CrCl_3$	0.138±.003	——-	———	0 175± 002.	———	0.1891±.0017	III

respectively. Since the targets were in a film form, the total attenuation were not required to be formed. From Table 2, it is seen that our values for the Ag metal film is closer to the theoretical values by Scofield [18] and to the experimental values by Salem *et al* [19]. Ideally, for all calculations the most probable value for K X-ray intensity ratio for silver is taken to be 0.212, which corresponds to the pure metal. It is seen that there is a significant difference in the values of K_β/K_α ratio, even for the same oxidation state of the X-ray emitting element. The K_β/K_α lines of non-transition elements owe their origins to the X-ray transitions between the inner 1s level and the outer valence level. When the atom takes part in chemical bonding, the valence AO (atomic orbitals) participate in the formation of MO's (molecular orbitals) of the compounds. The structure of these MO's is determined by the nature of the bonding of the component atoms. The chemical bonding type (ionic, metallic, covalent) affects the K X-ray fluorescence intensity ratios. The individual characteristics of the structure of the molecules, complexes and crystals also affect the K X-ray intensity ratios. A change in the chemical bond leads to a change in its valence electron density. The electron density decreases or increases depending on the type of bonding with the adjacent atoms in the molecule or crystal. Further, more molecules have different bond energies and different interatomic bond distances between ligands and the central atom. Different interatomic bond distances cause different interactions between ligands and central atoms. These effects play an important role in K X-ray transitions. We have also carried out the preliminary estimates of K X-ray yields using the Hartree – Fock wave functions computed by Clementi [20]. With the assumption of single particle transition, the dependence of any specific K X-ray line on the ionic state of the atom can be estimated by calculating the radial integral as given below.

$$W_\mu \alpha \int \varphi_f r^3 dr \varphi_i .$$

The calculated ratios W_{3p-1s}/W_{2p-1s} for Cr atoms are shown in Figure 4.

The calculated ratio increases with the increasing ionic charge of the atoms as shown by the experimental data for the

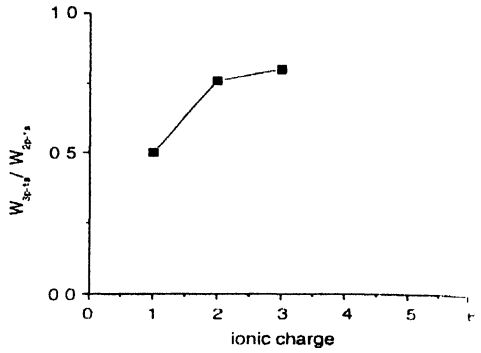


Figure 4. Calculated intensity ratio for Cr in different ionic charge stat

K_β/K_α ratio. Figure 5 gives the variation of Ag intensity rati with compounds, for photons, X-rays and protons.

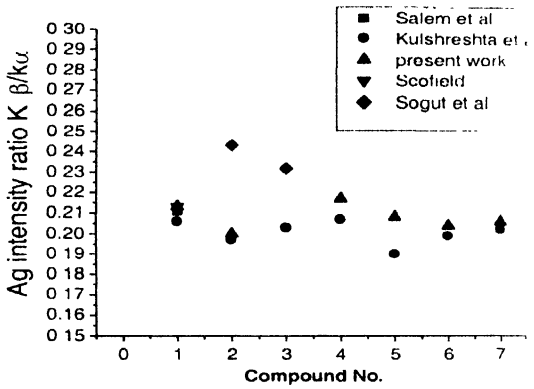


Figure 5. Variation of intensity ratios for different silver compou with photon excitation

It is seen that for Ag, the ratios decrease for protons th for photons. The values for the intensity ratios have be compared for Cr compounds in Table 1. It is seen that the valu by PIXE measurement are in agreement with Folkmann [1 values for the Cr compounds n confirmation with Scofiled o theory, the ratio increases with the increase in oxidation stat However with the Scofiled modified theory, the variation

Table 2. KX-ray intensity ratios of Ag and its compounds.

Compound	K_β/K_α photons EDXRF	Sogut *et al* [10] photons	Salem *et al* [19] photons	Theoretical Scofield [18] photons	K_β/K_α X-rays WDXRF	K_β/K_α protons PIXE
Ag metal	0.214± 002	0 217±.002	0.211± .001	0.213	0.200±.003	0.212±.003
AgCl	0.201±.003	0.231±.002	——		0.196±.003	0.193±.002
AgI	0.209±.001	——	——		0.212±.004	0.202±.003
Ag_2CO_3	0.205±.002	——	——		0.190±.003	0.198± 001
Ag_2SO_4	0.207±.003	——	——		0.193±.002	0.193±.003
AgBr	0.218±.001	——	—-		0.217±.001	0.195±.001

reverse and we have observed the same as seen in Figure 6, which gives the variation of Cr intensity ratios with oxidation state

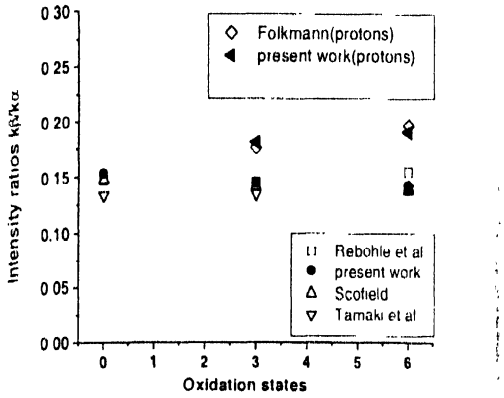


Figure 6. Cr intensity ratios for different oxidation states with photon and proton excitation

The chemical effects for the K X-ray lines by primary creation of a single vacancy in the K- shell as by the 2.5 MeV proton impact are determined by the transition probability from the valence electrons. It is seen that this ratio is different for the protons from that for the photons. These variations indicate the influence of the excited state configuration on the X-ray emission process. Since the K_α X-ray transition originates from $2p$ levels and the K_β X-ray transition originates from $3p$ levels, it is expected that the relative intensities of these transitions should depend on the number of L and M –shell vacancies in existence, at the time of X-ray emission. It is observed that K_β/K_α is increased for protons than for photons, indicating multiple L-shell ionization in case of PIXE and an increase in K_β line intensity leading to the increase in the ratio.

4. Conclusion

Ag and the compounds of Ag show variation in the values of K X ray intensity ratios even for the same oxidation state indicating the dependence of chemical environment to X-ray yields. For Cr compounds, the ratio for different valence state, is found to be more for PIXE than for EDXRF. Hence, it can be concluded that variation in intensity ratios depends on the mode of excitation. If a standard correlation between valence state and intensity ratios is obtained, it is possible to determine valence state of Cr, by measuring the intensity ratios of Cr and it is suggested to make a calibration for individual compounds before X-ray emission analysis is carried out to obtain accurate results.

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